String Method for the Study of Rare Events

Weinan E[1], Weiqing Ren[2], and Eric Vanden-Eijnden[2]
[1] *Department of Mathematics and PACM, Princeton University, Princeton, NJ 08544*
[2] *Courant Institute, New York University, New York, NY 10012*

We present a new and efficient method for computing the transition pathways, free energy barriers, and transition rates in complex systems with relatively smooth energy landscapes. The method proceeds by evolving strings, i.e. smooth curves with intrinsic parametrization whose dynamics takes them to the most probable transition path between two metastable regions in the configuration space. Free energy barriers and transition rates can then be determined by standard umbrella sampling technique around the string. Applications to Lennard-Jones cluster rearrangement and thermally induced switching of a magnetic film are presented.

PACS numbers: 05.10.-a, 02.70.-c, 82.20.Wt

The dynamics of complex systems are often driven by rare but important events (for a review see e.g. [1]). Well-known examples include nucleation events during phase transition, conformational changes in macromolecules, and chemical reactions. The long time scale associated with these rare events is a consequence of the disparity between the effective thermal energy and typical energy barrier of the systems. The dynamics proceeds by long waiting periods around metastable states followed by sudden jumps from one state to another.

Sophisticated numerical techniques have been developed to find the transition pathways and transition rates between metastable states in complex systems for which the mechanism of transition is not known beforehand [2, 3, 4]. With the exception of the transition path sampling technique [3], most of these methods seem to require that the energy landscape be relatively smooth. One typical example of such techniques is the nudged elastic band (NEB) method [4]. NEB connects the initial and the final states by a chain of states. The states move in a force field which is the combination of the normal component of the potential force and the tangential component of the spring force connecting the states. The spring force helps to evenly space the states along the chain.

In this paper we propose an alternative approach for computing transition pathways, free energy barriers, and transition rates. We sample the configuration space with strings, i.e. smooth curves with intrinsic parametrization such as arclength, or energy weighted arclength which connect two metastable states (or regions), A and B. The string satisfies a differential equation which by construction guarantees that it evolves to the most probable transition pathway connecting A and B. One can then perform an umbrella sampling of the equilibrium distribution of the system in the hyperplanes normal to the string and thereby determine free energy barriers and transition rates.

Consider the example of a system modeled by

$$\gamma\dot{q} = -\nabla V(q) + \xi(t). \tag{1}$$

where γ is the friction coefficient, $\xi(t)$ is a white-noise with $\langle \xi_j(t)\xi_k(0)\rangle = 2\gamma k_B T\delta_{jk}\delta(t)$. The metastable states are localized around the minima of the potential $V(q)$. Assuming $V(q)$ has at least two minima, A and B, we look for the minimal energy paths (MEPs) connecting these states. By definition, a MEP is a smooth curve $\varphi^\star$ connecting A and B which satisfies

$$(\nabla V)^\perp(\varphi^\star) = 0, \tag{2}$$

where $(\nabla V)^\perp$ is the component of ∇V normal to $\varphi^\star$. The MEPs are the most probable transition pathways for (1) since with exponentially high probability it is by these paths that the system switches back and forth between the states A and B under the action of a small thermal noise [5]. It is interesting to note that the solutions of (2) also provide relevant information about the Langevin equation

$$\begin{cases} \dot{q} = p, \\ \dot{p} = -\nabla V(q) - \gamma p + \xi(t). \end{cases} \tag{3}$$

Indeed, the metastable regions for (1) and (3) coincide, and the transition pathways for (3) can be easily determined from the transition pathways for (1) because they traverse the same sequence of critical points. As a result the transition rates for (3) for an arbitrary friction coefficient γ can be obtained by considering the high friction evolution equation (1) – see (10) below.

Let φ be a string (but not necessarily a MEP) connecting A and B. A simple method to find the MEP is to evolve φ according to

$$u^\perp = -(\nabla V)^\perp(\varphi), \tag{4}$$

where $u^\perp$ denotes the normal velocity of φ, since stationary solutions of (4) satisfy (2). For numerical purposes it is convenient to have a parametrized version of (4), keeping in mind however that the parametrization can be arbitrarily chosen since both (2) and (4) are intrinsic. Denote by $\varphi(\alpha, t)$ the instantaneous position of the string, where α is some suitable parametrization. Then we can rewrite (4) as

$$\varphi_t = -(\nabla V(\varphi))^\perp + r\hat{t}, \tag{5}$$

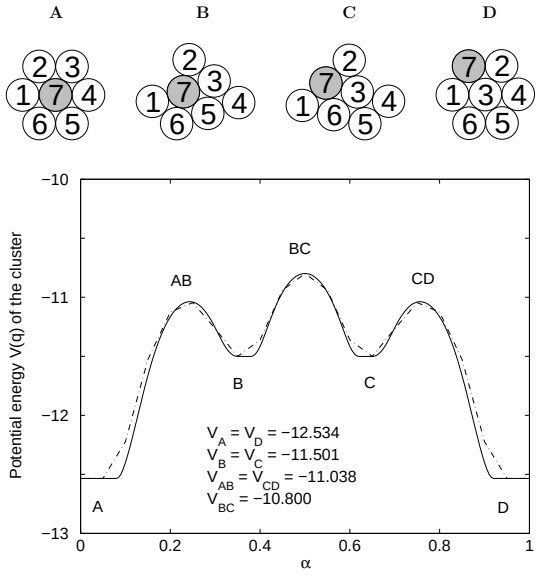

FIG. 1: Top figure: A transition pathway by which the central atom migrate to the surface in a seven-atom hexagonal Lennard Jones cluster in the plane. The pictures show successive configuration corresponding to local minima of potential energy along the path. Bottom figure: the potential energy along the path in natural units. The full line corresponds to a simulation with $N = 200$ discretization points along the string, and the dashed line, $N = 20$.

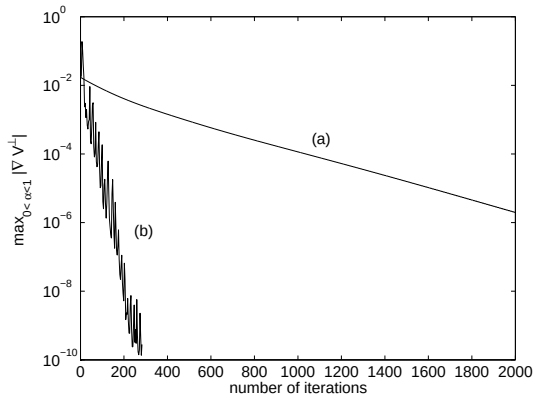

FIG. 2: The convergence history of the steepest descent method [(a)] and a limited memory version of Broyden's method [(b)] applied to the seven-atom cluster problem with $N = 200$ discretization points. We use $\max_{0\le\alpha\le1} |(\nabla V)^{\perp}|$ to measure accuracy.

where for convenience we renormalized time $t/\gamma \to t$, $(\nabla V)^{\perp} = \nabla V - (\nabla V \cdot \hat{t})\hat{t}$, and $\hat{t}$ is the unit tangent vector along φ, $\hat{t} = \varphi_\alpha/|\varphi_\alpha|$. The scalar field $r \equiv r(\alpha, t)$ is a Lagrange multiplier uniquely determined by the choice of parametrization. The simplest example is to parametrize φ by arclength normalized so that $\alpha = 0$ at A, $\alpha = 1$ at B. Then (5) must be supplemented by the constraint

$$(|\varphi_\alpha|)_\alpha = 0. \tag{6}$$

which determines r [6]. Other parametrizations can be straightforwardly implemented by modifying the constraint (6). For instance, a parametrization by energy weighted arclength which increases resolution at the transition states is achieved using the constraint $(f(V(\varphi))|\varphi_\alpha|)_\alpha = 0$, where $f(z)$ is some suitable monitor function satisfying $f'(z) < 0$. In addition, the end points of the string need not be fixed and other boundary conditions can be used.

Because of the intrinsic description of the string, it is very simple to implement an efficient algorithm which solves (5) using a time-splitting type of scheme. The string is discretized into a number of points which move according to the first term, $-(\nabla V(\varphi))^{\perp}$, at the right hand-side of (5). After a number of steps depending on the accuracy for the constraint (6), a reparametrization step is applied to reinforce (6). This costs $O(N)$ operations where N is the number of discretization points along the string. At the reparametrization step it is also convenient to change N according to the accuracy requirement for the representation of the string.

The method certainly bears some similarities with NEB since one can think of the introduction of the spring force in NEB as a way of ensuring equal-distance parametrization by a penalty method – NEB gives an evolution equation which, in the continuum limit, is similar to (5) but with r given by $r = \kappa\varphi_{\alpha\alpha} \cdot \hat{t}$ where κ is the artificial spring constant. As in other penalty methods, this numerical procedure introduces stiffness into the problem if the penalization parameter, here the elastic constant κ, is large and this limits the size of the time step. By using an intrinsic description, we eliminate this problem and speed up convergence. Furthermore we gain the ability of using other parametrizations in a simple and flexible way. Finally, there is no simple way to change the number of discretization points along the chain in NEB.

It is natural to ask how the string method compares to NEB in terms of performance. However such a comparison does not seem straightforward since it depends on the criteria. This is discussed in detail in [8].

As a first example we look at the dynamics of seven atoms interacting via Lennard-Jones potential on the plane. This example has been studied in detail in [7]. In equilibrium the seven atoms form an hexagon. We are interested in the process in which the atom at the center migrates to an external position. The MEPs are not unique for this problem. One example of MEP obtained via the string method is shown in figure 1; the critical points along this path coincide with the ones obtained in [7] by transition path sampling.

The string equation (5) essentially amounts to finding the MEPs by the method of steepest descent except that we are not working with any explicit object function to minimize. We can use advanced numerical techniques for

solving nonlinear equations [9] to accelerate convergence to the MEP. We have developed a limited memory version of Broyden's method where (5) is replaced by

$$\varphi_t = -G^{\perp}(\nabla V(\varphi))^{\perp} + r\hat{t}. \tag{7}$$

Here $G^{\perp}$ is a matrix determined on the fly to approximate the inverse of the Hessian in the perpendicular hyperplane; the approximation is based on the past history of φ and does not require to actually compute the Hessian (for details, see [8]). In figure 2, we compare the convergence history of the steepest descent method and the Broyden-accelerated method applied to the seven-atom cluster problem. The Broyden-accelerated method converges much faster.

Once the MEP $\varphi^{\star}(\alpha)$ has been determined using Broyden-accelerated string method, free energy barriers and transition rates can be computed by standard umbrella sampling of the equilibrium distribution of the system in $S^{\star}(\alpha)$, the hyperplane normal to $\varphi^{\star}(\alpha)$. Consider first the free energy difference along the string defined as $F(\alpha) - F(0) = -k_B T \ln(Z(\alpha)/Z(0))$ where

$$Z(\alpha) = \int_{S^{\star}(\alpha)} e^{-\beta V(q)} d^d q \tag{8}$$

is the partition function and $\beta = 1/k_B T$. Using the identity $\int \partial \ln Z/\partial\alpha d\alpha = \ln Z(\alpha)$, we obtain from (8)

$$F(\alpha) - F(0) = \int_0^{\alpha} \left\langle (\hat{t}^{\star}\cdot\nabla V)\left((\hat{t}^{\star}\cdot\varphi^{\star})_{\alpha'} - \hat{t}^{\star}_{\alpha}\cdot q\right)\right\rangle d\alpha'. \tag{9}$$

Here $\langle\cdot\rangle$ is the ensemble average with respect to equilibrium distribution restricted in the hyperplane $S(\alpha)$ and $t^{\star}$ is the unit tangent vector along $\varphi^{\star}$. (9) is similar to the standard thermodynamic integration [10] but is better suited for numerical purposes. In practice, we use ergodicity and replace the ensemble average in (9) by a time-average over the solution of an equation similar to (1) but restricted in the hyperplane $S(\alpha)$. Following Kramers original argument (see e.g. chap. 9 in [11]), the transition rate can be expressed in terms of the free energy as

$$k_{A\to B} = \frac{2\sqrt{\lambda_m|\lambda_s|}}{\pi\left(\gamma + \sqrt{\gamma^2 + 4|\lambda_s|}\right)} e^{-\beta\Delta F}, \tag{10}$$

where ΔF is free energy barrier along $\varphi^{\star}$

$$\Delta F = \max_{0\le\alpha\le 1} \left(F(\alpha) - F(0)\right), \tag{11}$$

and λ_m and λ_s are (inverse square of) characteristic time scales at the minimum and maximum of the free energy along the transition path; λ_m and λ_s are given by $|\varphi_\alpha|^{-2} F_{\alpha\alpha}$ evaluated at $\alpha = 0$ and $\alpha = \alpha_s$, respectively, where α_s is the value at which the maximum in (11) is attained [12].

The transition rates along the MEP obtained earlier for the seven-atom cluster were evaluated by the string method, and are summarized in table I.

The string method can easily be generalized to infinite dimensional dynamical systems by introducing an appropriate norm in phase-space. As an example, we consider the problem of thermally induced switching of a magnetic film. This problem is of great current interest in the magnetic recording industry [15]. (For an introduction to micromagnetism, see e.g. [13, 15]; thermally induced switching is studied in [14]). Landau-Lifshitz theory of micromagnetism provides an energy for a ferromagnetic sample Ω which after suitable nondimensionalization, reads

$$E[m] = A\int_{\Omega} |\nabla m|^2 d^3x + \int_{\Omega} \phi(m) d^3x + \int_{\mathbb{R}^3} |\nabla u|^2 d^3x, \tag{12}$$

where m is the magnetization distribution normalized so that $|m| = 1$. The three terms represent respectively energies due to exchange, anisotropy, and stray field. The potential u, defined everywhere in space, solves $\operatorname{div}(-\nabla u + m) = 0$, where m is extended as 0 outside Ω.

Various switching pathways for (12) were obtained using the string method: two examples are shown in figure 3 and the energy along these paths is shown in figure 4. These paths illustrate two generic mechanisms for switching in magnetic films. Path (a), which is more favorable in thin samples, proceeds by domain wall motion, interior rotation, and switching of the edge domains. Path (b), which is more favorable for thicker films, proceeds by vortex nucleation, invasion of the sample and vortex expulsion.

In conclusion, transition pathways and transition rates for complex systems with a relatively smooth energy landscape can be determined efficiently by evolving strings instead of points in configuration space. The in-

	$k_{A\to B} = k_{D\to C}$	$k_{B\to A} = k_{C\to D}$	$k_{B\to C} = k_{C\to B}$
string	5.023×10^{-13}	1.425×10^{-4}	1.211×10^{-6}
exact	4.969×10^{-13}	1.423×10^{-4}	1.206×10^{-6}

TABLE I: The rates for the various subprocesses in the transition shown in figure 1 in the seven-atom cluster problem. We use natural units and the same parameters as in [7] (for which, e.g., $k_B T/\Delta E_{A\to B} = 0.033$ and $\gamma/2\sqrt{|\lambda_s|} = 0.012$ – low friction limit). The rates $k_{A\to B}$, $k_{B\to A}$, and $k_{B\to C}$ correspond respectively to the rates for the subprocesses $C_0^0 \to C_1^4$, $C_1^4 \to C_0^0$, and $C_1^4 \to C_1^3$ identified in [7]. The values labeled "string" were obtained by the noisy string method using (9), (11), and (10). The values labeled "exact" were obtained using (10) and (13), by identifying minima and saddle points along the transition path, computing the corresponding energy barrier ΔE, and evaluating all the eigenvalues of the Hessian at the minima and the saddle points from the Hessian itself.

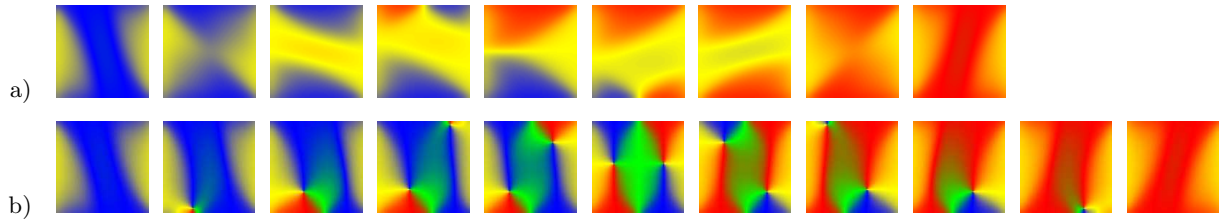

FIG. 3: Two of the paths [(a) and (b)] followed by the magnetization vector m during a switching. The pictures show the succession minimum – saddle – ... – saddle – minimum. The out-of-plane component of m is very small (less than 10^{-2}) during the switching and we only plot its in-plane component with color coding: blue = right, red = left, yellow = up, green = down. For both paths, we used $N = 200$ discretization points along the string.

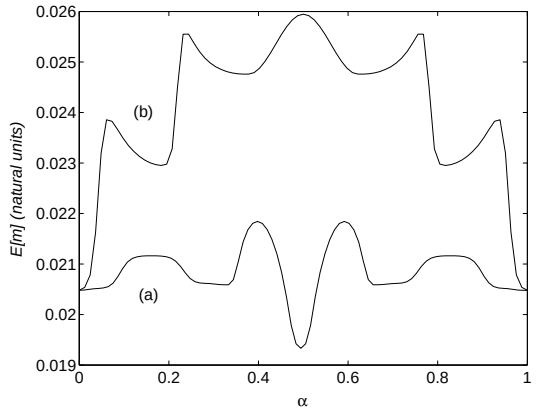

FIG. 4: The magnetic energy along the two paths [(a) and (b)] shown in figure 3

trinsic parametrization of the string leads to a simple and efficient algorithm for the numerical solution of its evolution equation, and permits to sample the configuration space in regions that otherwise would be practically inaccessible by standard Monte-Carlo methods.

We thank Roberto Car and Bob Kohn for helpful discussions. The work of E is supported in part by NSF grant DMS01-30107.

[1] P. Hänggi, P. Talkner, and M. Borkovec, Rev. Mod. Physics **62**, 251 (1990).

[2] I. V. Ionova, E. A. Carter, J. Chem. Phys. **98**, 6377 (1993); R. Olender and R. Elber, J. Chem. Phys. **105**, 929 (1996); Theochem.–J. Mol. Struc. **398**, 63 (1997); A. Michalak and T. Ziegler, J. Phys. Chem. A **105**, 4333 (2001); D. Passerone and M. Parrinello, Phys. Rev. Lett. **87**, 108302 (2001).

[3] C. Dellago, P. G. Bolhuis, F. S. Csajka, and D. Chandler, J. Chem. Phys. **108**, 1964 (1998).

[4] H. Jónsson, G. Mills, and K. W. Jacobsen, in: Classical and Quantum Dynamics in Condensed Phase Simulations, B. J. Berne *et al.* eds, World Scientific, 1998; G. Henkelman and H. Jónsson, J. Chem. Phys. **113**, 9978 (2000).

[5] M. I. Freidlin and A. D. Wentzell, Random Perturbations of Dynamical Systems, 2nd ed. Springer, 1998.

[6] In this case r is given explicitly by

$$r = \alpha \int_0^1 \nabla V \cdot \hat{t}_{\alpha'} d\alpha' - \int_0^\alpha \nabla V \cdot \hat{t}_{\alpha'} d\alpha'.$$

[7] C. Dellago, P. G. Bolhuis, and D. Chandler, J. Chem. Phys. **108**, 9236 (1998).

[8] W. E, W. Ren, and E. Vanden-Eijnden, in preparation.

[9] C. T. Kelley, Iterative Methods for Linear and Nonlinear Equations, SIAM, 1995.

[10] D. Frenkel, B. Smit, Understanding Molecular Simulations. From Algorithms to Applications, Academic Press, San Diego, 1996.

[11] C. W. Gardiner, Handbook of Stochastic Methods, 2nd ed. Springer, 1985.

[12] In the small temperature limit, the free energy difference can also be expressed as

$$\Delta F = \Delta E - k_B T \ln \sqrt{\frac{\det H_m^\perp}{\det H_s^\perp}}, \qquad (13)$$

plus higher order terms in $k_B T$, where ΔE is the energy barrier along the MEP, and $H_m^\perp$ and $H_s^\perp$ are the Hessian matrix in the hyperplane perpendicular to the MEP evaluated at the minimum and the transition state (saddle) respectively. In the same limit λ_m and λ_s are the eigenvalues of the Hessian corresponding to the eigenvectors parallel to the MEP evaluated at the minimum and the transition state respectively.

[13] A. Aharoni, Introduction to the Theory of Ferromagnetism. Oxford Univ. Press, 1996.

[14] H.-B. Braun, Phys. Rev. Lett. **71**, 3557 (1993); Phys. Rev. B **50**, 16485 (1994); Phys. Rev. B **50**, 16501 (1994); D. V. Berkov, *J. Magn. Mag. Mat.* **186**, 199 (1998); W. E, W. Ren, and E. Vanden-Eijnden, submitted to: J. Appl. Phys. (2002).

[15] R. P. Cowburn, Phil. Trans. Roy. Soc. London A **358**, 281 (2000).